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Tetracyanoethylene Addition to Iron Tricarbonyl Complexes of Substituted Cyclooctatetraenes. Regioselectivity Considerations during Formation of the 2,3,4,10-Tetrahapto Adducts

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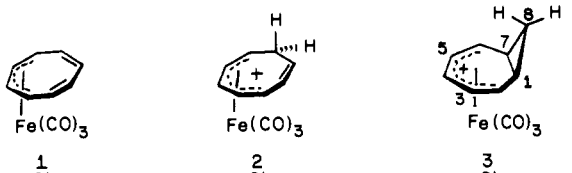
Abstract: The cycloaddition of tetracyanoethylene to a number of cyclooctatetraeneiron tricarbonyls occurs via an unusual 1,3 bonding process with formation of η^4 products in which the iron atom is both σ and π bonded. Although the reaction gives every indication of being general, the site of initial attack by the uniparticulate electrophile is markedly influenced by electronic factors. Thus, methylcyclooctatetraeneiron tricarbonyl is shown to yield two complexes arising from attack at the γ (71%) and δ (21.5%) ring carbons (relative to the substituent). For the phenyl case, attack at the α position (39%) is seen to be competitive with bonding at the γ (16%) and δ (23%) sites. As concerns carbomethoxyl substitution, this electron-withdrawing group directs the electrophile preferentially α (23%) and β (64%). The inference to be drawn from the methoxyl example is that bonding to the γ carbon is kinetically preferred. In benzocyclooctatetraeneiron tricarbonyl, the carbon atom adjacent to the site of benzo fusion is attacked exclusively as it is in protonation. Oxidation of the adducts with ceric(IV) ion furnishes dihydrotetracyanotriquinacenes in high yield and this route will likely be serviceable for the convenient preparation of unusually substituted triquinacenes. A tentative mechanistic scheme which rationalizes all of the data is presented.

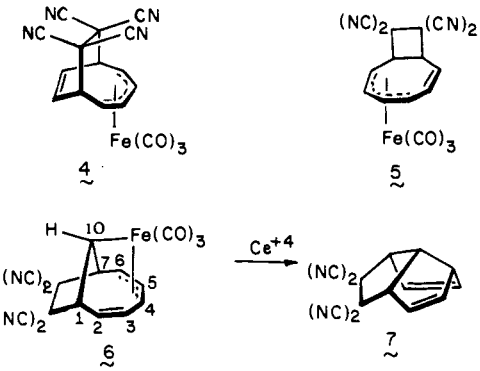
The manner in which the chemical properties of cycloolefinic ligands are modified through coordination to a metal center has been the subject of intensive investigation during the last two decades since the discovery of ferrocene. This high level of interest has been fostered by the numerous unique transformations which have been uncovered, some mechanistic implications of which continue to challenge both inorganic and organic chemists. Sometimes discoveries of new and novel reactions are not without the attendant problems of proper visualization and analysis of the events. As a direct consequence, improper or erroneous interpretations are occasionally advanced. Cyclooctatetraeneiron tricarbonyl (**1**) is a case in point. Several conflicting claims surrounded the early investigations of the chemistry of **1** subsequent to its initial synthesis in 1959.[2] For example, its protonation was first studied by Rausch and Schrauzer and the resulting species was considered to be the monocyclic structure **2**.[3] This assignment was quickly corrected by Wilkinson and coworkers who established by ^{1}H NMR techniques that the bicyclo[5.1.0]octadienyliron tricarbonyl cation **3** is actually formed under these conditions.[4] More recent work by Brookhart has revealed that low-temperature (−120°) protonation of **1** in FSO_3H-SO_2F_2 does in fact lead initially to the ring opened cyclooctatrienyliron tricarbonyl cation (**2**);[5] upon warming of such solutions, clean first-order electrocyclization to **3** occurs with a $\Delta F^{\ddagger}_{-60°}$ of 15.7 kcal/mol. Proton attack trans to the iron atom is kinetically preferred, with the entering hydrogen (deuterium) ultimately occupying the endo H_8 position in **3**.[4] Protonation of cyclooctatetraene itself is now recognized to lead to a homotropylium ion in which the electrophile is similarly endo oriented.[6] Interestingly, these results contrast with the exo stereochemistry attending protonation of cyclooctatetraenemolybdenum tricarbonyl,[7] and with the



1 2 3

ultimate fate of the ruthenium and osmium analogs of **1** under similar conditions.[8]

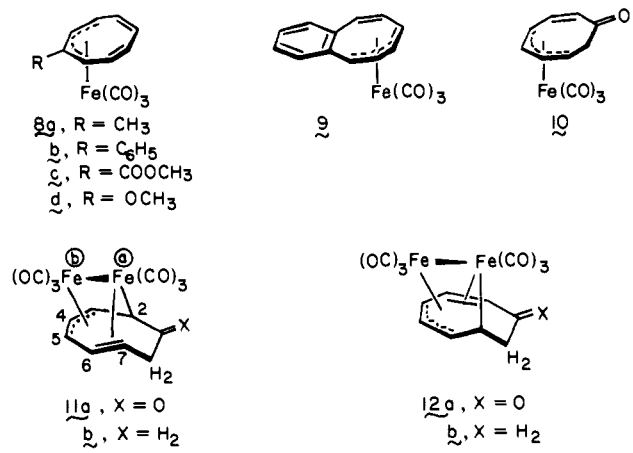
The structure of the 1:1 adduct resulting from cycloaddition of TCNE to **1** has also been the subject of considerable speculation. Initially, attention was focused on its so-called "nonbonded" 1,3-diene moiety and a $(4 + 2)\pi$ bonding scheme leading to **4** was envisaged.[4,9,10] This point of view was further nurtured by the exceptionally high reactivity of **1** toward this dienophile compared with related η^6-cyclooctatetraene complexes and by the rather insoluble nature of the adduct which purportedly precluded ^{1}H NMR analysis. Subsequently, Green and Wood argued in favor of a $(2 + 2)\pi$ reaction and formulated the product as the 1,2 adduct **5**.[11] Recent reinvestigations of this reaction[12-14] have concurred in their conclusion that the novel σ,π-bonded iron complex **6** is in fact formed in an intriguing 1,3-cycloaddition process, a conclusion which is now firmly supported by ^{1}H NMR and X-ray crystallographic findings.[13] Since uncoordinated cyclooctatetraene reacts with TCNE via its [4.2.0]bicyclic valence tautomeric form in classical Diels–Alder fashion,[15] the formation of **6** (96% yield) clearly illustrates the noteworthy modification of reactivity which can accompany transition metal complexation. Moreover, ceric ion oxidation of **6**[12,13] serves to provide high yield access to **7**, an important intermediate in the efficient synthesis of chiral 2-substituted triquinacene derivatives.[16]



Two aspects of the chemistry of **6** became the goals of the study described herein. The first of these was mechanistic in nature and concerned the influence of electronic factors on the kinetic preference for 1,3 capture of the TCNE and on the regioselectivity of this reaction. The second objective was to assess the preparative aspects of the conversion of substituted derivatives of **1** into more heavily functionalized congeners of **7** for possible elaboration into multiply substituted triquinacenes.[16] At the time when this study was approaching completion, a report by Green, Heathcock, and Wood appeared[14] in which the reactions of the bromo, methyl, and phenyl derivatives of **1** with TCNE are described. Our experience with two of the same complexes has convinced us that the work of the Bristol group is incomplete, the most insoluble isomer seemingly having been the only one characterized in each instance. Their claim that lone 1,3 adducts are uniquely formed when R = CH_3 or C_6H_5 should be treated with reservation.

Results

Preparation of the Complexes. A procedure similar to that employed by Anet[17] was used in the preparation of **8a.** Reaction of phenyl- and carbomethoxycyclooctatetraenes with equimolar amounts of diiron enneacarbonyl in refluxing hexane for approximately 1 hr provided dark red crystals **8b** and **8c,** respectively. The benzo complex **9** was synthesized according to the procedure of Elix and Sargent[18] as modified by Stucki.[19] When methoxycyclooctatetraene in dry ether was heated at reflux for 3 hr with $Fe_2(CO)_9$ and the crude reaction mixture directly distilled, complex **8d** was isolated as dark red needles in moderate yield. However, when silica gel chromatography was utilized for purification purposes, there was obtained in addition to **8d**



(32%) two other air stable complexes, both of which were subsequently shown to arise from vinyl ether hydrolysis during chromatography. The fraction of intermediate polarity (10%) was a yellow solid which in its infrared spectrum clearly revealed ketonic carbonyl bands (1650 and 1635 cm^{-1}) in addition to the metal carbonyl absorptions (2065, 1985, and 1970 cm^{-1}). On the basis of its ^{1}H NMR spectrum [$\delta_{TMS\ (CDCl_3)}$ 6.23 (m, 2), 5.63 (m, 2), 3.54 (br t, $J \approx$ 8 Hz, 1), 2.95 (m, 2), and 2.38 (t, 1)], the predominant valence tautomer is tentatively formulated as that which is conjugatively uncomplexed, i.e., **10.**

The large red prisms obtained in 5% yield upon ether elution were found to be identical with the complex of formula $C_8H_8OFe_2(CO)_6$ previously prepared by King[20] through reaction of cyclooctatrienone with triiron dodecacarbonyl. Although King was aware from ^{1}H NMR considerations that this complex was perhaps of a type structurally related to that of $C_8H_{10}Fe_2(CO)_6$ derived from 1,3,5-cyclooctatriene, his misassignment of the latter structure prompted a more detailed analysis of the ketone derivative. Cotton and Edwards recently established the correct formulation of $C_8H_{10}Fe_2(CO)_6$ to be the dissymmetric structure depicted by **11b** (or **12b**).[21] Interestingly, this molecule in solution was found to exhibit rapid exchange between the two possible enantiomorphous forms (**11b** $\rightleftarrows$ **12b**).[22]

The crystal and molecular structure of the ketone complex has been determined by X-ray crystallographic techniques.[23] The crystals proved to be triclinic of space group $P\bar{1}$, a = 11.93(1), b = 8.258(8), c = 7.729(8) Å; 3687 unique data in the $\pm h \pm kl$ hemisphere were collected on a Picker 4 circle automated diffractometer using graphite monochromatized Mo Kα radiation to sin θ/λ = 0.7°. Both iron coordinates were established from the Patterson map and the medium atoms were subsequently located by atomic superposition. A final unweighted discrepancy index of 0.032 was realized. As with **11b** and **12b,** the $Fe_2(CO)_6$ moiety adopts a "sawhorse" geometry with Fe_a residing 2.10, 2.23 and 2.24 Å from C_2, C_6, and C_7, respectively, and Fe_b being 2.15, 2.05, and 2.12 Å removed from C_3, C_4, and C_5, respectively. The involvement of Fe_b is unquestionably that of *trihapto*-allyl coordination, whereas Fe_a is seen to be σ bonded to C_2 and π complexed to the C_6–C_7 double bond.

Thus, the ketone in the solid state is **11a** and not **12a.** The causative factors underlying the preferred bonding of Fe_a to C_2 as in **11a** rather than C_7 as in **12a** are not known at this time. However, the possible control of preferred metal coor-

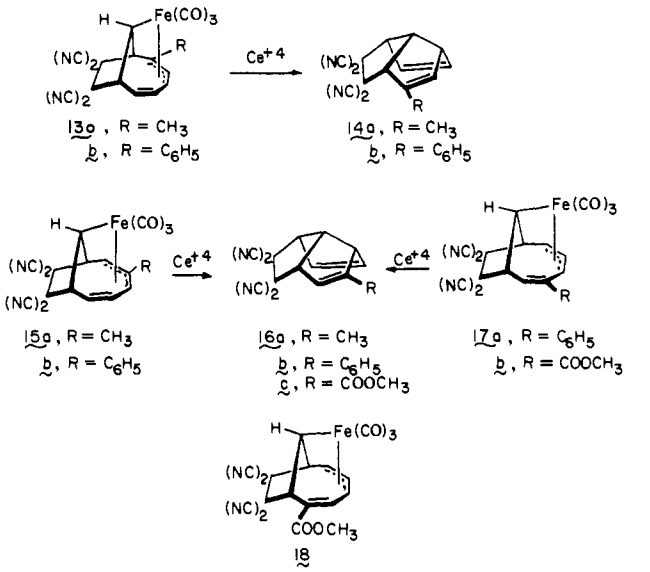
Table I. Chemical Shift Data for the TCNE Adducts (δ Values)

Compd	Solv	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_{10}	Other	Apparent coupling constants, Hz
6	DMSO-d_6	3.94 (ddd)	5.76 (dd)	6.6 (ddd)	4.4–4.68 (m)	4.9–5.2 (m)		4.4–4.68 (m)	1.56 (dd)		$J_{1,2}$ = 4.5; $J_{1,3}$ = 2; $J_{2,3}$ = 11; $J_{3,4}$ = 9; $J_{1,10}$ = 6.5; $J_{7,10}$ = 11.5
13a	$(CD_3)_2CO^a$	4.0	5.88	6.66	4.42	5.1		4.68	1.9		$J_{1,2}$ = 5; $J_{2,3}$ = 9; $J_{1,10}$ = 6; $J_{7,10}$ = 12
15a	DMSO-d_6	3.78–3.99 (m)	5.86 (dd)	6.66 (ddd)	4.38–4.74 (m)		4.92–5.21 (m)	4.38–4.74 (m)	1.7 (dd)	2.13 (s)	$J_{1,2}$ = 5.5; $J_{1,3}$ = 2; $J_{2,3}$ = 12; $J_{1,10}$ = 6; $J_{7,10}$ = 12
13b	$(CD_3)_2CO$	3.96–4.16 (m)	6.02 (dd)	6.77 (ddd)	4.72 (dd)	5.64 (d)		5.30 (d)	2.14 (dd)	7.32–7.6 (m,3) 7.74–7.94 (m,2)	$J_{1,2}$ = 5; $J_{1,3}$ = 2; $J_{2,3}$ = 11; $J_{4,5}$ = 10; $J_{1,10}$ = 7; $J_{7,10}$ = 12
15b	$(CD_3)_2CO$	3.92–4.12 (m)	6.04 (dd)	6.98 (ddd)	5.18–5.42 (m)		5.58 (d)	4.80–5.08 (dd)	1.90 (dd)	7.30–7.70 (m)	$J_{1,2}$ = 4.5; $J_{1,3}$ = 2; $J_{2,3}$ = 10; $J_{3,4}$ = 8.5; $J_{6,7}$ = 8; $J_{1,10}$ = 7; $J_{7,10}$ = 12
17a	$(CD_3)_2CO$	4.18 (dd)	6.0 (d)		4.52–4.92 (m)	5.22–5.5 (m)		4.52–4.92 (m)	1.88 (dd)	7.28–7.68 (m)	$J_{1,2}$ = 4.8; $J_{1,10}$ = 6.5; $J_{7,10}$ = 11
17b	$CDCl_3$	3.98 (dd)	6.78 (d)		4.73		5.2	4.32 (ddd)	1.6 (dd)	3.54 (s)	$J_{1,2}$ = 5; $J_{5,7}$ = 2; $J_{6,7}$ = 5.5; $J_{1,10}$ = 7; $J_{7,10}$ = 12
18	$CDCl_3$	4.28 (d)		7.96 (d)	5.01–5.42 (m)	4.69 (dd)	5.01–5.42 (m)	4.58 (dd)	1.97 (dd)	3.82 (s)	$J_{3,4}$ = 9; $J_{5,6}$ = $J_{4,5}$ = 8.5; $J_{6,7}$ = 7; $J_{1,10}$ = 7.2; $J_{7,10}$ = 11
19	$(CD_3)_2CO$	3.97 (m)	6.01 (dd)	6.73 (dd)		5.36 (d)	4.96 (dd)	4.59 (dd)	1.69 (dd)	3.66 (s)	$J_{1,2}$ = 4.5; $J_{1,3}$ = 2; $J_{2,3}$ = 11; $J_{5,6}$ = 8.5; $J_{6,7}$ = 7; $J_{1,10}$ = 7; $J_{7,10}$ = 11

[a] Data taken from ref 14.

dination by electronic and dipole contributions in the ligand is intimated and warrants further study.

Preparation and Oxidative Degradation of the Adducts. Treatment of **8a** with an equimolar amount of TCNE in methylene chloride solution at room temperature led to the rapid precipitation of a pale yellow solid. Isolation and spectral characterization (Table I) of this substance showed it to be the 6-methyl isomer **13a.** Specifically, the H_6 signal for **6** which is centered at δ 5.0 is seen to be lacking in the spectrum of **13a,** a methyl resonance appearing instead at 1.80. Confirmatory proof of this assignment is available in the form of an X-ray crystal structure analysis.[24] Additional amounts of **13a** could be isolated from the mother liquor (71% total yield), fractional crystallization also affording **15a** (21.5%). The ^1H NMR spectrum of this complex shows signals which require the methyl substituent to be at the 5 position (Table I).



Upon oxidation with ceric ammonium nitrate, these two adducts led to the isomeric dihydrotriquinacenes **14a** and **16a,** respectively. As seen from the data summary in Table II, the olefinic proton on the methyl substituted double bond in **16a** resonates at higher field than that in **14a,** presumably owing to enhanced shielding by the proximal nitrile functions.

When the cycloaddition was performed in benzene solution and the product mixture directly analyzed by ^1H NMR (DMSO-d_6) using Pulse Fourier Transform techniques, the **13a:15a** ratio was seen to be 3:1 (integration of methyl peaks). Direct oxidative degradation with Ce^{4+} and subsequent ^1H NMR assay of the dihydrotriquinacene mixture again established the 3:1 composition (now **14a:16a**). These values agree closely with the 3.3:1 isolated yields achieved with methylene chloride as solvent.

When **8b** was allowed to react with TCNE in analogous fashion (C_6H_6 solution), three adducts were isolated in pure form. The isomer bearing a phenyl substituent at C_2 was not detected, but we do not discount the possibility that this complex was formed in low yield and lost during the rather involved separation procedure. Structural assignment to the trio of products follows again from their distinctive ^1H NMR spectra (Table I). In the case of the 3-phenyl isomer (**17a,** 39%), H_2 appears as a doublet (J = 4.8 Hz) at δ 6.0. The magnitude of this spin-spin interaction compares well with the $J_{1,2}$ value of the parent system. Another characteristic absorption is a doublet of doublets at 4.18 which has been assigned to H_1 on the strength of the apparent coupling constants $J_{1,10}$ = 6.5 Hz and $J_{1,2}$ = 4.8 Hz. The api-

Table II. Chemical Shift Data for the Tetracyano Dihydrotriquinacenes (δ Values)

Compd	Solv	Aliphatic protons	Olefinic protons	Other
7	$(CD_3)_2CO$	3.85–4.48 (m)	H_3, H_5 6.14–6.38 (m) H_2, H_6 5.73–5.96 (m)	
14a	$CDCl_3$	3.75–4.2 (m)	H_3 5.84 (br s) H_5 6.15 (br d, J = 5 Hz) H_6 4.72 (d, J = 5 Hz)	1.92 (s)
16a	$CDCl_3$	3.55–4.12 (m)	H_2 5.32 (br s) H_5 6.37 (br d, J = 5.5 Hz) H_6 5.80 (d, J = 5.5 Hz)	1.87 (s)
14b	$CDCl_3$	H_1, H_7, H_{10} 4.0–4.3 (m) H_4 4.54–4.74 (m)	H_3 6.44 (br s) H_5 6.24 (d, J = 5 Hz) H_6 5.81 (d, J = 5 Hz)	7.24–7.64 (m)
16b	$CDCl_3$	H_1, H_7, H_{10} 4.04–4.3 (m) H_4 4.34–4.50 (m)	H_2 5.95 (d, J = 2 Hz) H_5 6.38 (br d, J = 5.8 Hz) H_6 5.82 (d, J = 5.8 Hz)	7.33–7.76 (m)
16c	$CDCl_3$	4.1–4.4 (m)	H_2 6.67 (br s) H_5 5.86 (d, J = 5.5 Hz) H_6 6.54 (d, J = 5.5 Hz)	3.83 (s)
20	$(CD_3)_2CO$	H_1, H_7 4.50 (m) H_{10} 3.86 (t, $J_{1,10} = J_{1,7}$ = 8.2 Hz)	H_2, H_6 6.04 (dd, $J_{1,2} = J_{6,7}$ = 2 Hz) H_3, H_5 6.29 (dd, $J_{2,3} = J_{5,6}$ = 5.5 Hz)	3.21 (s)

cal hydrogen attached to the carbon bearing σ-bonded iron (H_{10}) is seen at 1.88.

The 5-phenyl isomer (**15b,** 23%) shows revealing peaks at 5.88 (d, J = 8 Hz) attributed to H_6 and at 1.9 (dd, J = 7 and 12 Hz) arising from H_{10}. Ceric ion oxidation of **17a** and **15b** led to the identical dihydrotriquinacene derivative (**16b**) as expected from their substitution patterns.

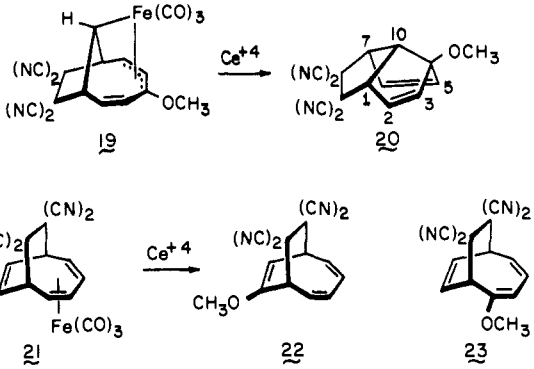
The more diagnostic spectral features of the 6-phenyl isomer (**13b,** 16%) are the signals characteristic of H_2 and H_3 at δ 6.02 and 6.77, both of which possess splitting patterns typical of parent complex **6,** and the doublets at 5.64 and 5.30 due to H_5 (J = 10 Hz) and H_7 (J = 12 Hz), respectively. Its oxidative degradation produced **14b** which as expected exhibited a lower field β-styrenyl olefinic signal than **16b.**

Repetition of the TCNE cycloaddition under Green's conditions (CH_2Cl_2 solution) and direct ^1H NMR analysis of the crude product revealed the presence of all of the above isomers. Direct oxidation afforded a mixture of **14b** and **16b** in a 2.7:1 ratio. Seemingly therefore, solvent dependence seems not be a complicating factor. Temperature effects were not studied.

The reaction of TCNE with **8c** either in methylene chloride or benzene solution led to the isolation of **17b** and **18** in 64 and 23% yield, respectively. The observation that **17b** lacks the signal due to H_3 while exhibiting a low-field doublet (J = 5 Hz) at δ 6.78 ascribable to H_2 and a doublet of doublets (J = 5 and 7 Hz) at 3.98 due to H_1 convincingly denotes the site of carbomethoxyl substitution. Noteworthily, positioning of this group at C_2 as in **18** causes both H_3 and H_1 to be shifted to lower field, H_3 the more so. Oxidative removal of the $Fe(CO)_3$ moiety from **17b** gave rise to **16c** in 86% yield.

As concerns the methoxyl substituted complex **8d,** analogous reaction with TCNE led to a complex mixture of adducts as seen by the appearance of at least six methoxyl signals in the ^1H NMR spectrum. Although this unpurified mixture proved to be air sensitive (extensive decomposition occurring at 0° over some time), it proved possible to isolate in 31.5% yield the most insoluble component. The yellow solid was identified as **19,** the unique C_4 positioning of the methoxyl group following from the absence of the signal characteristic of H_4, the prevailing coupling constants (Table I) as revealed by double irradiation studies, and by oxidative degradation to **20.** This dihydrotriquinacene derivative possesses four olefinic protons, thereby requiring methoxyl to be bonded to one of the sp^3-hybridized carbons. However, positions 1, 7, and 10 can readily be dismissed as the sites of substitution by spin decoupling measurements at 100 MHz. Irradiation of the H_{10} signal (δ 3.21), for example, collapses the absorption due to H_1 and H_7 (δ 4.50) to a narrow multiplet. Furthermore, because H_1 and H_7 are overlapping, a symmetrical substitution pattern is revealed, a criterion uniquely satisfied by methoxyl attachment to C_4. This conclusion was substantiated by saturation of the H_2, H_6 (6.04) and H_1, H_7 (4.50) signals which causes collapse respectively of the H_1, H_7 pattern and the H_2, H_6/H_3, H_5 multiplet pair to individual doublets. In the latter experiment, the H_{10} resonance is also simplified to a broadened singlet.

Immediate attempted purification of the mother liquors from the above crystallization did not achieve separation of the several components.[25] A second attempt was made approximately 1 month later after storage at 0° during that period. On this occasion it proved possible to isolate from the very dark residue a small amount of complex **21** (stereochemistry of iron tricarbonyl group assumed). Structural assignment to **21** follows from its ^1H NMR spectrum and conversion to triene **22,** an enol ether isomeric with the major product (**23**) formed upon direct TCNE addition to



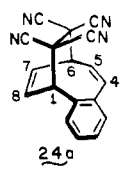
uncomplexed methoxycyclooctatetraene.[26] We have no evidence that **21** is formed directly in the cycloaddition reaction and cannot dismiss the possibility that it is a secondary transformation product.

Analogous treatment of benzo complex **9** with TCNE gave a mixture of adducts which because of their insolubility and instability toward attempted purification were oxidized directly. Fractional recrystallization sufficed to separate the resulting three oxidation products. The major component was identified as the 1,4 adduct **24a** on the basis of

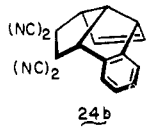
its characteristic ^1H NMR spectrum which shows three sets of olefinic signals at δ 6.97 (d, H_4), 6.50 (dd, H_8), and 6.1 (m, H_5 and H_7) in addition to a readily discernible pair of bridgehead methines at 4.83 (d, H_1) and 4.32 (dd, H_6). Double resonance studies clearly revealed H_6 to be significantly coupled to H_5 and H_7, and H_1 to interact substantially only with H_8. The absence of mutual coupling between the methine hydrogens serves to dismiss in particular those structural assignments which contain a tetracyanocyclobutane ring. That the 1,4 addition has proceeded in the indicated manner to give **24a** follows from the chemical shifts of the methine and olefinic protons.

The ^1H NMR spectrum of the second crystalline product (a second $C_{18}H_{10}N_4$ isomer) exhibited two olefinic doublets of unit intensity centered at 6.15 and 5.63 which are mutually coupled to the extent of 5.8 Hz[27] and two upfield multiplets at 4.6–4.85 (area 1) and 4.2–4.55 (area 3) in addition to the aromatic signal (4 H). The nonequivalency of the two olefinic protons, the great similarity of the spectrum to that of **7**,[12,13] and the presence of four sp^3-bonded protons rule out alternative (2 + 2) or (4 + 2) structures and satisfy in detail those features required by the dihydrobenzotriquinacene assignment **24b.**

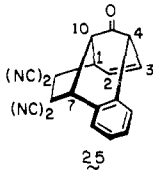
Unexpectedly, the minor component analyzed for $C_{19}H_{10}N_4O$ and consequently insertion of carbon monoxide had occurred as well. The ir spectrum of this ketonitrile displayed intense peaks at 2260 and 1750 cm^{-1} for the cyano and carbonyl groups. Its ^1H NMR spectrum exhibited six well defined proton signals in addition to the aromatic multiplet of area 4, the chemical shifts and multiplicity of which reveal the bonding pattern shown in formula **25.** Evi-



24a



24b



25

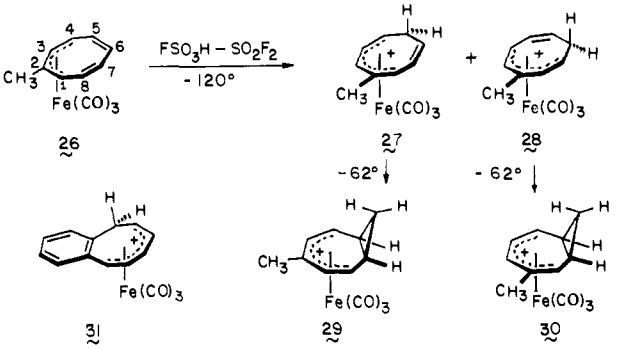
dently, during the oxidative removal of the iron tricarbonyl groups in the 1,3-cycloadduct a carbonyl moiety is interposed between C_4 and C_{10} (see Discussion). Of the two low-field absorptions, the multiplet at δ 6.4–6.8 is assigned to H_3 while the apparent doublet (additional fine coupling is present) centered at 5.96 is attributed to the only other olefinic proton (H_2). That the H_4 doublet ($J_{3,4}$ = 5.5 Hz) is likewise at rather low field (5.40) is evidence of the simultaneous bonding of C_4 to both the carbonyl carbon and the benzene ring. The benzylic nature of H_7 is reflected in its chemical shift (4.7). Long-range coupling of H_1 to H_7 as a result of their W-plan arrangement is also in evidence. It is anticipated that H_1 and H_{10} would appear at highest field and on this basis the δ 4.12 doublet is tentatively assigned to H_1 and the 3.9 multiplet to H_{10}.

Discussion

It comes as no surprise that coordination of a cyclic polyolefin to a tricarbonyliron unit will substantially alter the reactivity of the ligand. There have been relatively few instances, however, where the precise role of the metal atom is clearly defined, particularly where electrophilic processes are concerned. Data are available to suggest that complexation serves initially to deactivate the olefin,[28] although subsequent stabilization of cationic intermediates is clearly important.[29,30] The recent reports of several groups[31-33] agree that most "cycloaddition" reactions of TCNE with transition metal complexed ligands occur because of the ability of the tetranitrile to function as a uniparticulate electrophile.[34] That TCNE is also capable of reacting with certain noncoordinated molecules via electrophilic pathways involving transient intervention of zwitterionic intermediates is now also well established.[35]

Therefore it appears reasonable that the initial step in the bonding of TCNE to a cyclooctatetraeneiron tricarbonyl involves development of dipolar character. Initial attack can occur either exo or endo to the metal atom at a coordinated or uncomplexed double bond. In the present set of circumstances, the structure of the adduct requires preferential initial bonding of TCNE to the exo surface of the ring. This finding is in agreement with the demonstration of exo approach for protonation.[4,5] Entry of TCNE trans to the iron atom would seemingly rule out such alternative mechanistic possibilities as that in which direct one-electron transfer between Fe10 and TCNE operates initially.

The position of electrophilic attack is considerably more difficult to establish, although the presence of a ring substituent as in the present study can be expected to serve as a guiding factor. Were attack to occur at a coordinated site, the $Fe(CO)_3$ group would be forced to migrate simultaneously to a free double bond. In contrast, bonding at an uncoordinated π bond would lead directly to a complexed pentadienyl cation. In this connection, Brookhart, Davis, and Harris[5] have shown that low-temperature (−120°) protonation of methylcyclooctatetraeneiron tricarbonyl, which exists chiefly as isomer **26** under these conditions,[17] undergoes protonation competitively only at C_6 (33%) and C_7 (66%) to give **27** and **28,** respectively. Upon warming to −62°, these two complexes undergo disrotatory ring closure with formation of **29** and **30.** Consequently, **26** and by in-



26 27 28

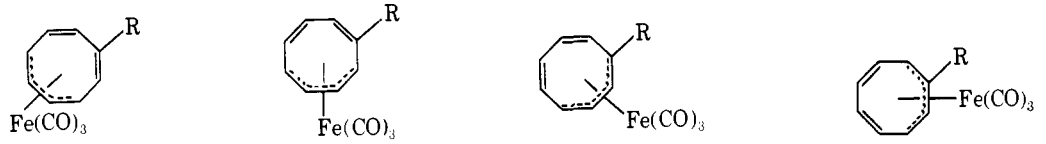
31 29 30

ference **1** as well undergo kinetically controlled electrophilic attack at the central carbon atoms of the uncomplexed diene moiety.

Merk and Pettit[36] have observed that **9** is protonated in sulfuric acid to give only the pentadienyl cation **31,** but similar data on the site selectivity of the protonation process are not available.

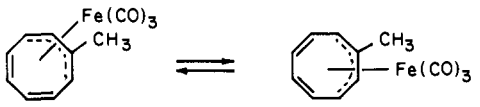
In contrast to the Brookhart study, the TCNE additions reported herein were conducted at 25°. A comprehensive study of the pmr spectra of various monosubstituted cyclooctatetraeneiron tricarbonyl derivatives by Bock[37] does, however, provide useful information on the prevailing tautomeric equilibria at room temperature (Table III). In brief, electron withdrawing groups are seen to force the iron residue to the side of the ring opposite the substituent, perhaps because the double bonds adjacent to the R group experience the greatest level of electron deficiency. Alkyl and heteroatomic groups give a more complex distribution. The relevant aspects of these equilibria to the current problems are obvious. However, considering that the free energy of activation for valency tautomerism in **26** at −125°, a process which interconverts **26a** and **26b,** is only 7.5 kcal/mol,[17] direct extrapolation of the data in Table III to electrophilic reactions of these complexes (which are likely more energy

Table III. Tautomeric Equilibria for Various Monosubstituted Cyclooctatetraeneiron Tricarbonyl Complexes at Room Temperature[37]



A B C D

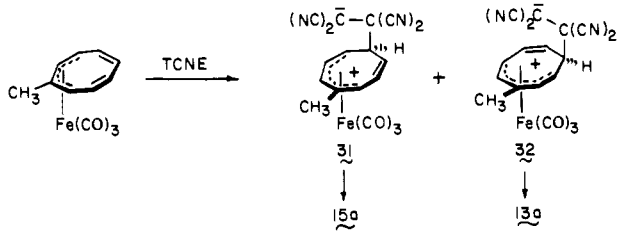
R	A	B	C	D
COOR'	0.9	0.1		
CN	0.9	0.1		
$COCH_3$	0.5	0.5		
CHO	0.5	0.5		
OCH_3	~0.4	~0.4	?	?
C_6H_5	0.5			0.5
CH_2OH	0.25	0.25		0.5
CH_3	0.2			0.8



26a 26b

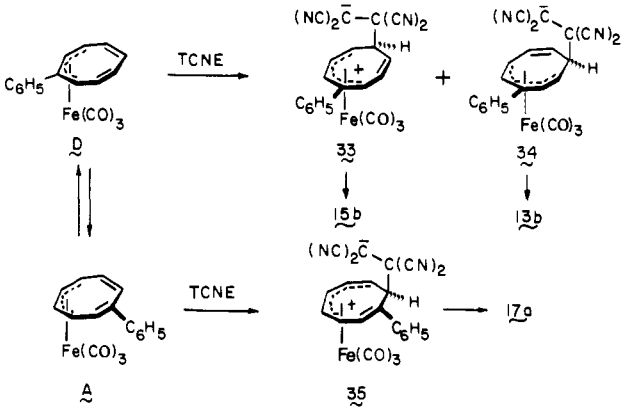
demanding) must be made with utmost caution (Curtin-Hammett principle). For **1** and **9**, the experimentally determined energies of activation are 7.2[38] and 18.6 kcal/mol.[19]

Despite the assumptions mandated by the above considerations and the symmetry of the TCNE molecule which can potentially becloud considerations of the initial point of attack, it is possible to define a theoretically plausible reactivity scheme. For the present cases, increased differentiation between competing pathways follows if the transition state energy differences are in the same direction as the ground state energy differences and of an equal or greater order of magnitude. In the case of methylcyclooctatetraeneiron tricarbonyl, for example, the interpretation can be advanced that valence tautomer **26** is also kinetically most reactive at room temperature with the result that zwitterions **31** and **32** are produced. Regioselectivity considerations require that **32** be formed at a rate greater than three times that leading to **31** to account for the relative proportions of **13a** (71%) and **15a** (21.5%). Perhaps coincidentally,

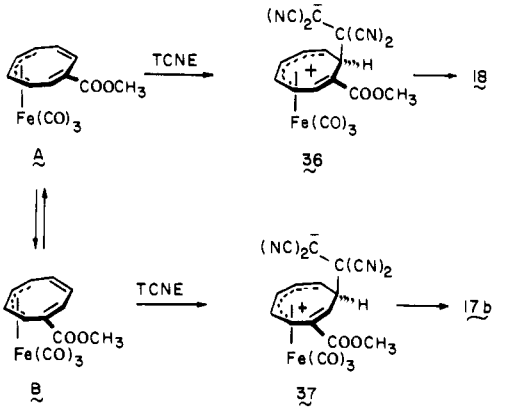


the **31**:**32** ratio closely approximates that of **27** and **28** realized upon low-temperature protonation.[39]

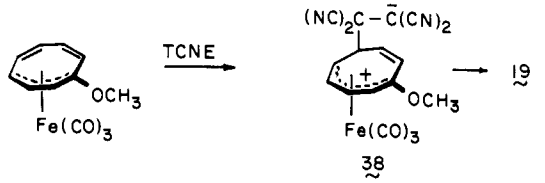
In the phenyl-substituted series, the formation of **15b** (23%) and **13b** (16%) can similarly be rationalized in terms of intermediates **33** and **34**. The proportion of the two cycloadducts agains suggests a kinetic preference for formation of dipolar structural type **34**. As Bock has noted,[37] phenyl substitution apparently provides a significantly higher concentration gradient of isomer A (Table III) than does a methyl group. If valence tautomer A possesses a reactivity level comparable to that of D, then 1,3 bonding to this complex should be recognizable in the product array. The isolation of **17a** indicates that these conditions seemingly do operate. Because attack of the electrophile at the phenyl-substituted carbon in A is disfavored for steric (and perhaps electronic) reasons, selective bonding to the only other remaining internal uncomplexed trigonal carbon as depicted in **35** is realized.



For carbomethoxy derivative **8c**, the energy costs of positioning the electronegative group on the complexed diene (Table III) and on the pentadienyl cation are assumedly sufficiently large to preclude reaction through isomers C and D. As concerns the remaining two tautomers, however, the experimental data implicates less populous species B as precursor to the major adduct (**17b**, 64%). This may be a direct consequence of the electronic state of affairs in the pair of dipolar intermediates, the carbomethoxy group being cross-conjugated with the pentadienyl cation moiety in **37** but not in **36**.



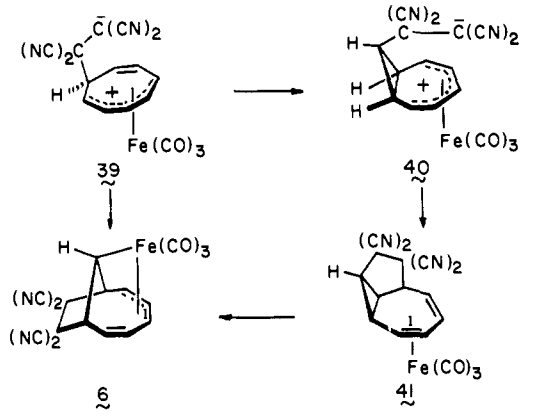
With **8d**, bonding of TCNE to valence tautomer C is seen to be favorable perhaps because the stabilization accorded the pentadienyl cation unit by a 1-methoxyl substituent as in **38** makes this reaction channel less endothermic than alternative electrophilic pathways.[41] The positional selectivity for attack of TCNE on benzocyclooctatetraeneiron tricar-



38

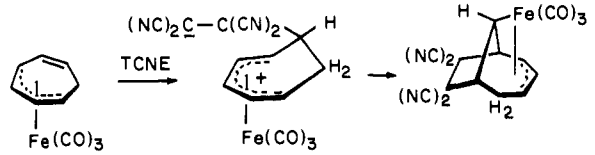
bonyl (**9**) parallels that for proton addition (cf. **31**).

With these structural elements now tentatively identified, we wish to comment briefly on the mechanism by which the iron atom becomes σ bonded to carbon. Two speculative interpretations that might be advanced are direct collapse of the initial zwitterion (e.g., **39**) to give 1,3 adduct directly or prior valence isomerization to **40**, charge annihilation with formation of **41**, and subsequent bond reorganization to furnish **6**. As noted previously, cations **27** and **28** which are



39 40 6 41

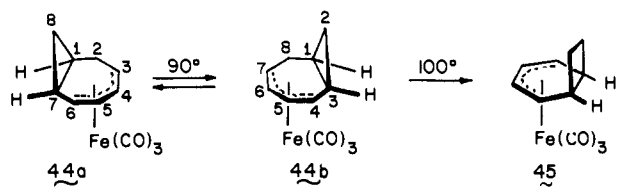
structurally related to **39** undergo disrotatory closure with remarkable facility.[5] That such a valence isomerization need not be a prerequisite to closure of **39** to **6** is indicated by the behavior of cycloheptatrieneiron tricarbonyls toward TCNE. An analogous reaction occurs with these lower homologs to give high yields of 1,3 adducts such as **43**.[12,28,30,31] Of course, the possibility is quite real either



42 43

that the rate of collapse of **39** to **6** exceeds that of the conversion of **39** to **40** or that the **39** → **40** isomerization is reversible. The consequences of the latter phenomenon are obvious.

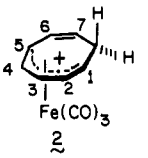
A further point is that the necessarily ready rearrangement of **41** to **6** lacks precedent. Hypothetical intermediate **41** is seen to be a bicyclo[5.1.0]octa-2,4-dieneiron tricarbonyl complex and as such is a derivative of **44**. Aumann has recently shown by deuterium labeling studies that **44** is capable of isomerization at 90°.[42] When heated to 100° in degassed heptane for long periods of time, **44** slowly isomerizes to **45**.[43] No σ,π-$Fe(CO)_3$ complexes result. Since there



44a 44b 45

is every reason to believe by inference that **41** should also possess good inherent stability, we prefer to think that it does not intervene in the formation of **6**.

We may now ask why **39** is predisposed for carbon–carbon bond formation at C_2. While our understanding of the details of charge distribution in metal complexed cations remains incomplete,[44] Brookhart's detailed ^1H NMR study[5] of cation **2** does provide some important clues. It can be

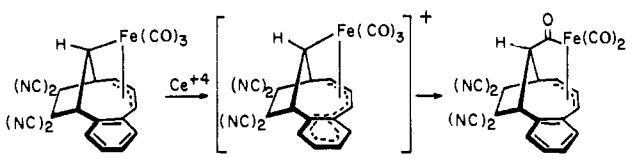


2

H_1, H_5	δ 4.58
H_2, H_4, H_6, H_7	δ 5.95
H_3	δ 6.9

seen that the protons at the 2, 4, 6, and 7 positions appear at relatively low field. Since such deshielding can be construed to mean that electron deficiency is greatest at these ring positions, then kinetically controlled bonding (intramolecular) of the pendant carbanion center to C_2 can be regarded as a reasonable mechanistic prerogative.

The ability of the benzo system to undergo facile carbonyl insertion is somewhat remarkable. Generally, such reactions require high carbon monoxide pressures and somewhat elevated temperatures.[14,45] Since both **24b** and **25** appear to arise from the same σ,π-iron complex (**46**), it seems



46 47 48

24b 25

that the stereoelectronic benefit of enhanced cationic stabilization uniquely available to **47** may facilitate migration of the bridgehead carbon to provide **48** at a rate competitive with direct oxidative degradation. The merit of this mechanistic interpretation remains to be assessed at the experimental level.

In conclusion, the data obtained herein indicate not only that novel 1,3 bonding of TCNE to cyclooctatetraeneiron tricarbonyls is a general reaction type, but also that substituents have a profound and varied influence on the site selectivity which operates during uniparticulate electrophilic attack. Thus, stereoelectronic factors are of meaningful importance in the chemistry of metal carbonyl complexed cyclic polyolefins. In the specific case of TCNE, subsequent oxidative removal of the iron atom leads to variously substituted tetracyanodihydrotriquinacenes which should prove to be serviceable precursors to triquinacenes not readily obtainable by other methods.

Experimental Section

Melting points are corrected and boiling points are uncorrected. Proton magnetic resonance spectra were obtained on Varian A60-A, Varian HA-100, and Jeolco MH-100 spectrometers; apparent splittings are given in all cases. Infrared spectra were determined on Perkin-Elmer Model 137 and 467 instruments. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Phenylcyclooctatetraeneiron Tricarbonyl (8b). To 60 ml of hexane was added 1.8 (0.01 mol) of phenylcyclooctatetraene and diiron enneacarbonyl (3.64 g, 0.01 mol) and the mixture was refluxed under nitrogen for 1 hr. Solvent was evaporated from the cooled reaction mixture and the residue was subjected to chromatography on Florisil (110 g) using ether–pentane (1:5) as eluent. The red fraction was collected to give 1.6 g (50%) of **8b** as dark red crystals. A sample was sublimed at 53° and 0.01 mm for analysis:

mp 65-65.5°;[46] $\delta_{TMS\,(CDCl_3)}$ 7.25 (br s, 5) and 5.3 (br s, 7). Anal. ($C_{17}H_{12}FeO_3$) C, H.

Carbomethoxycyclooctatetraeneiron Tricarbonyl (8c). A solution of carbomethoxycyclooctatetraene (810 mg, 5 mmol) in 30 ml of hexane was treated with 1.82 g (5 mmol) of diiron enneacarbonyl and the mixture was heated at reflux for 1.2 hr under nitrogen. The solvent was evaporated and the residue was chromatographed on Florisil (75 g). Hexane elution afforded 1.2 g (80%) of **8c** as dark red crystals, mp 51-53°. Sublimation at 48° (0.01 mm) raised the mp to 52.5-53°. Anal. ($C_{13}H_{10}FeO_5$) C, H.

Reaction of Methoxycyclooctatetraene with $Fe_2(CO)_9$. Procedure A. A mixture of diiron enneacarbonyl (3.6 g, 0.01 mol) and methoxycyclooctatetraene (1.34 g, 0.01 mol) in dry ether (50 ml) was refluxed for 3 hr in an atmosphere of nitrogen. The solution was cooled, filtered, and evaporated to give a red oil which was chromatographed on silica gel. Petroleum ether (30-60°) eluted a red oil (1.25 g) which consisted of a mixture of unreacted methoxycyclooctatetraene and its iron tricarbonyl complex **8d.** The uncomplexed ether was removed by bulb-to-bulb distillation and the residue was rechromatographed to provide 860 mg (32%) of **8d** as large dark red needles: mp 46-46.5° (from pentane); $\nu_{max\,(Nujol)}$ 2060 and 1985 cm^{-1}; $\delta_{TMS\,(CDCl_3)}$ 5.52-5.45 (m, 7, olefinic) and 3.50 (s, 3, methoxy). Anal. ($C_{12}H_{10}FeO_4$) C, H.

Continued elution with petroleum ether-ether (5:1) afforded an orange fraction from which 250 mg (9.7%) of **10** was isolated as yellow needles: mp 104-105° dec (from ether-pentane); $\nu_{max\,(Nujol)}$ 2065, 1985, and 1655 cm^{-1}; $\delta_{TMS\,(CDCl_3)}$ 6.23 (m, 2, olefinic), 5.63 (m, 2, olefinic), 3.54 (br t, $J \approx 8$ Hz, 1), 2.95 (m, 2), and 2.38 (t with additional coupling, 1). Anal. ($C_{11}H_8FeO_4$) C, H.

Ultimately, elution with ether gave a red fraction from which 200 mg (5%) of **11a** as large red prisms was obtained: mp 159-161° (from methylene chloride-ether); $\nu_{max\,(Nujol)}$ 2060, 1995, 1950, and 1655 cm^{-1}; $\delta_{TMS\,(CDCl_3)}$ 5.0 (t, J = 7.5 Hz, 1), 4.45 (m, 2), 3.95 (t, J = 8.5 Hz, 1), 3.32 (m, 1), 2.58 (d, J = 6 Hz, 2), and 2.25 (d, J = 8.5 Hz, 1). Anal. ($C_{14}H_8Fe_2O_7$) C, H.

Procedure B. To a rapidly stirred solution of methoxycyclooctatetraene (3.0 g, 0.022 mol) in 100 ml of hexane was added diiron enneacarbonyl (9.0 g, 0.025 mol) and the mixture was refluxed under nitrogen for 50 min. The cooled reaction mixture was filtered, the filtrate was concentrated, and the residual dark red oil was distilled twice in a short-path still. There was obtained 2.7 g (45%) of **8d,** bp 85-90° (0.03 mm), which crystallized on standing, mp 45-46°.

TCNE Addition to 8a. To a rapidly stirred solution of **8a** (2.5 g, 9.7 mmol) in methylene chloride (250 ml) was added 1.24 g (9.7 mmol) of tetracyanoethylene in one portion under nitrogen. The dark red solution became yellow within 1 min with precipitation of a pale yellow solid. After 1 hr the yellow product was isolated by filtration and air dried to give 2.25 g of **13a,** mp > 270° (dec starts at 195°). Anal. ($C_{18}H_{10}FeN_4O_3$) C, H, N.

The mother liquor was evaporated to yield a further 1.48 g of yellow solid. This solid was stirred for 5 hr with methylene chloride (100 ml) and filtered to provide an additional 400 mg of **13a.** From the soluble fraction there was obtained 1.01 g of yellow solid which by ^1H NMR analysis was essentially pure **15a.** Recrystallization from methylene chloride-pentane furnished the analytical sample (805 mg): mp 120° dec. Anal. ($C_{18}H_{10}FeN_4O_3$) C, H, N.

Oxidative Degradation of 13a. A mixture of **13a** (200 mg, 0.52 mmol) and ceric ammonium nitrate (4 g, 7.3 mmol) in methanol (30 ml) was stirred for 96 hr at room temperature under nitrogen. A small amount (56 mg) of unreacted **13a** was removed by filtration, the solvent was evaporated, and the residue was shaken with water (15 ml) and methylene chloride (15 ml). The layers were separated and the aqueous phase was extracted further with methylene chloride (3 × 15 ml). The combined organic layers were washed with brine, dried, and evaporated to leave 89 mg (70%) of **14a,** mp 134-135° (from aqueous acetone). Anal. ($C_{15}H_{10}N_4$) C, H.

Oxidative Degradation of 15a. A 300-mg sample of **15a** was oxidized with ceric ammonium nitrate in comparable fashion for 120 hr. The product was isolated as a gum (202 mg) which was crystallized from methanol to give white crystals, mp 173-175°, of **16a** (91 mg, 47.5%). Anal. ($C_{15}H_{10}N_4 \cdot 2CH_3OH$) C, H.

TCNE Addition to 8b. To a solution of **8b** (5.0 g, 0.0156 mol) in 40 ml of benzene under nitrogen was added a solution of TCNE (2.0 g, 0.0156 mol) in 250 ml of benzene. The stirred mixture gradually turned from dark red to yellow green with precipitation of a yellow solid. After 50 min, this solid was isolated by filtration and air dried to give pure **17a** (1.97 g), mp > 250° dec, upon recrystallization from aqueous acetone. Anal. ($C_{23}H_{12}FeN_4O_3$) C, H, N.

The mother liquors were evaporated under reduced pressure and the residue was treated with 50 ml of benzene. The mixture was refluxed briefly then cooled to give a yellow solid which was filtered, washed consecutively with benzene (5 ml) and ethanol (5 ml), and dried to yield a further 770 mg (total 39.2%) of **17a.** The mother liquors were evaporated to dryness, the solid was taken up in 50 ml of ethanol, and the solution was warmed nearly to reflux. After cooling to room temperature for 1 hr the solid was separated and the process was repeated a further two times. The total ethanol insoluble fraction so collected was washed with a little ethanol and recrystallized from hexane-benzene (3:1) to give pure **15b** (1.6 g, 23%): mp > 260° dec. Anal. ($C_{23}H_{12}FeN_4O_3$) C, H, N.

The ethanol mother liquors were evaporated to dryness and the residue was triturated with 20 ml of hexane. The remaining solid was stirred with a few milliliters of ethanol, filtered, and air dried to give crude **13b.** Recrystallization from benzene-hexane gave the pure 6-phenyl isomer (1.107 g, 16%): mp > 260° dec. Anal. ($C_{23}H_{12}FeN_4O_3$) C, H, N.

3-Phenyl-8,8,9,9-tetracyanotricyclo[5.2.1.$0^{4,10}$]deca-2,5-diene (16b). A. Oxidation of 17a. Ceric ammonium nitrate (8.43 g, 15.4 mmol), **17a** (0.50 g, 1.12 mmol), and ethanol (75 ml) were stirred together at room temperature under nitrogen for 24 hr. The solvent was partially removed under reduced pressure and the residue was diluted with water (150 ml). Extraction with methylene chloride (3 × 50 ml) gave 360 mg (100%) of **16b** as white crystals: mp 199-200° (from ethanol). Anal. ($C_{20}H_{12}N_4$) C, H.

B. Oxidation of 15b. By a similar method, 0.50 g of **15b** was converted to **16b** (302 mg, 84%) during 24 hr. This product proved identical by ^1H NMR analysis and melting point with the tetracyano dihydrotriquinacene isolated above.

2-Phenyl-8,8,9,9-tetracyanotricyclo[5.2.1.$0^{4,10}$]deca-2,5-diene (14b). Treatment of a solution of **13b** (450 mg, 1.005 mmol) in 75 ml of ethanol with 7.59 g (13.8 mmol) of ceric ammonium nitrate as described above for 24 hr furnished 1.9 g (61.5%) of **14b,** mp 159-160°, after recrystallization from aqueous ethanol. Anal. ($C_{20}H_{12}N_4$) C, H.

Reaction of 8b with TCNE Followed by Direct Oxidation. Iron complex **8b** (407 mg, 1.27 mmol) was dissolved in methylene chloride (20 ml) and a solution of TCNE (162 mg, 1.27 mmol) in this solvent (40 ml) was added in one portion under nitrogen. After 15 min, the solvent was evaporated and the residual yellow solid was dissolved in ethanol (80 ml) under nitrogen. Ceric ammonium nitrate (8 g) was added, ethanol was removed in vacuo after 68 hr, and the residue was taken up in water (50 ml) and extracted with methylene chloride (6 × 25 ml). The combined organic extracts were dried and evaporated to give the crude mixture of **14b** and **16b.** ^1H NMR analysis showed the ratio of these isomers to be 1:2.7.

A small portion (40 mg) of this mixture was subjected to preparative TLC purification. With ether-pentane (4:1) as eluent, there was obtained 18 mg of **16b** (R_f = 0.5), mp 196-198°, and 9 mg of **14b** (R_f = 0.43), mp 159-160°. Each was isomerically pure by ^1H NMR.

TCNE Addition to 8c. Tetracyanoethylene (965 mg, 7.45 mmol) was added to a stirred solution of **8c** (2.25 g, 7.45 mmol) in methylene chloride (200 ml) under nitrogen. Stirring was continued for 1 hr during which time the red colored solution turned yellow. Removal of the solvent in vacuo gave a yellow solid, ^1H NMR analysis of which revealed the presence of two isomers in the ratio of 1:3.7. Crystallization from hexane-acetone furnished 1.4 g of pale yellow crystals, mp > 260° (with onset of decomposition at 160°), of pure **17b.** Anal. ($C_{19}H_{10}FeN_4O_5$) C, H, N.

Addition of more hexane to the mother liquors caused precipitation of yellow solid (1.3 g) which proved to be a 1:1 mixture of **17b** and **18.** These isomers could be separated by TLC on silica gel using ether-pentane (70:30) as eluent. The amount of **17b** isolated (R_f = 0.54) raised the total isolated yield to 64%. There was also obtained 81 mg (23%) of **18** (R_f = 0.4): mp 120° dec. Anal. ($C_{19}H_{10}FeN_4O_5$) C, H, N.

When this reaction was repeated in benzene solution, ^1H NMR analysis of the total crude reaction mixture showed the **17b:18**

ratio to be 3:1.

3-Carbomethoxy-8,8,9,9-tetracyanotricyclo[5.2.1.0^{4,10}]deca-2,5-diene (16c). Complex **17b** (1.0 g, 2.33 mmol), ceric ammonium nitrate (16 g, 29 mmol), and methanol (150 ml) were stirred together under a nitrogen atmosphere for 48 hr at room temperature. The usual work-up afforded 582 mg (86%) of **16c** as colorless crystals: mp 132–133° (from hexane–methanol). Anal. ($C_{16}H_{10}N_4O_2$) C, H, N.

TCNE Addition to 8d. The iron complex (2.7 g, 0.01 mol) was dissolved in 200 ml of methylene chloride, and tetracyanoethylene (1.28 g, 0.01 mol) was added in one portion. After being stirred for 1 hr at room temperature under nitrogen, the reaction mixture was evaporated under reduced pressure to leave a pale yellow solid. This material was slurried with ether (15 ml), filtered, and air dried to afford 1.25 g (31.5%) of **19** as a pale yellow solid: mp 110° dec (from methylene chloride). Anal. ($C_{18}H_{10}FeN_4O_4$) C, H, N.

Removal of solvent from the filtrate gave a pale yellow gum (2.7 g), ^{1}H NMR analysis of which showed it to contain a number of products (five visible methoxyl signals). Attempted separation at that time proved unsuccessful. However, when purification was attempted at a later (ca. 1 month) date, it proved possible to isolate 71 mg of **21:** mp 180° dec (from methylene chloride); $\delta_{TMS\ ((CD_3)_2CO)}$ 5.86–6.25 (m, 2), 5.5 (d, 1), 3.64–4.72 (m, 4), and 3.74 (s, 3). Anal. ($C_{18}H_{10}FeN_4O_4$) C, H, N.

4-Methoxy-8,8,9,9-tetracyanotricyclo[5.2.1.0^{4,10}]deca-2,5-diene (20). Complex **19** (500 mg) was stirred together with ceric ammonium nitrate (10 g) and methanol (75 ml) at room temperature for 36 hr. Solvent was removed and the orange residue was shaken with water (50 ml) and methylene chloride (50 ml). The layers were separated and the aqueous phase was extracted with a further quantity of methylene chloride (2 × 50 ml). The combined extracts were washed with water, dried, and evaporated to furnish 225 mg (69%) of **20:** mp 215.5–217° (from methylene chloride). Anal. ($C_{15}H_{10}N_4O$) C, H, N; *m/e* calcd 262.0854; Found, 262.0859.

Oxidative Degradation of 21. Complex **21** (30 mg) was oxidized with ceric ammonium nitrate (700 mg) in the predescribed fashion to give 15 mg (77%) of **22:** mp 136–137°; $\delta_{TMS\ ((CD_3)_2CO)}$ 6.1–6.4 (m, 4), 5.32 (dd, 1), 4.0–4.4 (m, 2), and 3.67 (s, 3). Anal. *m/e* calcd, 262.0854; found, 262.0859.

TCNE Addition to Methoxycyclooctatetraene. Methoxycyclooctatetraene (300 mg) was treated with tetracyanoethylene (287 mg) in benzene under nitrogen for 24 hr to yield adduct **23:** mp 146–147° (from methylene chloride–hexane); $\delta_{TMS\ ((CD_3)_2CO)}$ 5.77–6.45 (m, 4), 5.52 (d, 1), 3.93–4.28 (m, 2), and 3.67 (s, 3). Anal. ($C_{15}H_{10}N_4O$) C, H, N.

TCNE Addition to 9. Benzocyclooctatetraeneiron tricarbonyl (1.25 g, 4.26 mmol) was dissolved in benzene (15 ml) and treated with a solution of tetracyanoethylene (545 mg, 4.26 mmol) in benzene (60 ml) at room temperature under nitrogen with efficient stirring. The color of the mixture rapidly changed to a dark brown and a precipitate formed. After 16 hr the suspension was filtered and the yellow-gray residue was washed with benzene. This material was dissolved in hot acetone and decolorized with activated carbon. There was isolated 1.56 g (87%) of bright yellow powder: $\delta_{TMS\ ((CD_3)_2CO)}$ 7.2–7.95 (m, 4, aryl), 5.06–5.7 (m, H_5 and H_6), 4.55–4.9 (m, H_4 and H_7), 3.75–4.2 (m, H_1), and 1.2–1.7 (m, H_{10}). Attempted recrystallization from acetone led to decomposition and consequently the substance (1.265 g, 3.0 mmol) was directly oxidized with ceric ammonium nitrate (25.0 g, 45 mmol) in 95% ethanol (100 ml). After 24 hr, the customary work-up procedure was followed to give an oily residue. Crystallization from methanol yielded a solid (0.40 g, 47.3%) which was separated by fractional recrystallization into the less soluble **24a** (0.25 g) and more soluble **24b** (0.10 g).

For **24a:** mp 197.5–199°; $\delta_{TMS\ ((CD_3)_2CO)}$ 7.46 (m, 4, aryl), 6.97 (d, J = 8 Hz, H_4), 6.50 (dd, J = 6 and 4 Hz, H_8), 6.1 (m, 2, H_5 and H_7), 4.83 (d, J = 4 Hz, H_1), and 4.32 (dd, J = 5.5 and 4.5 Hz, H_6). Double irradiation of the 4.32 and 4.83 peaks greatly simplified the 6.1 and 6.50 multiplets, respectively. Spin decoupling of H_5 and H_7 collapsed the 6.97 and 6.50 signals to singlets. Anal. ($C_{18}H_{10}N_4$) C, H; *m/e* calcd, 282.0906; found, 282.0908.

For **24b:** mp 168–169°; $\delta_{TMS\ ((CD_3)_2CO)}$ 7.2 (m, 4, aryl), 6.15 (d, J = 5.8 Hz, 2, olefinic), 5.63 (d, J = 5.8 Hz, 2 olefinic), 4.6–4.85 (m, 1, methine), and 4.2–4.55 (m, 3, methine). Anal. ($C_{18}H_{10}N_4$) C, H.

The residue from the methanol mother liquor, which crystallized upon evaporation of the solvent, was recrystallized from chloroform to yield the ketone **25** (189 mg, 14%): mp 236–237°; $\nu_{max\ (KBr)}$ 2260 and 1750 cm^{-1}; $\delta_{TMS\ ((CD_3)_2CO)}$ 7.2–7.8 (m, 4), 6.4–6.8 (m, H_3), 5.96 (d with additional fine coupling, J = 6 Hz, H_2), 5.40 (d, J = 5.5 Hz, H_4), 4.7 (m, H_7), 4.12 (d with additional fine coupling, J = 3.5 Hz, H_1), and 3.9 (m, H_{10}). Anal. ($C_{19}H_{10}N_4O$) C, H, N; *m/e* calcd, 310.0855; found, 310.0832.

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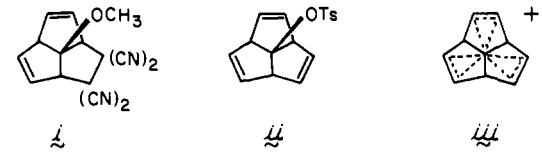

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Some Facile Syntheses of Optically Active 2-Substituted Indanones, Indanols, Tetralones, and Tetralols via Their Chromium Tricarbonyl Complexes

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Abstract: 1-Indanone- and 1-tetralonetricarbonylchromium were resolved into optically pure forms and their absolute configurations ascertained. These complexes can be used as precursors to chiral arene compounds difficult or impossible to prepare by other routes. Thus, examples of the syntheses of 2-methyl-1-indanone and 2-methyl-1-tetralone, *cis*- and *trans*-2-methyl-1-indanols, and 2-methyl-1-tetralols are shown. All these reactions are stereospecific.

In the last few years, the use of organometallic complexes in the synthesis of novel organic compounds has become common.[1] However, the utilization in this manner of arene tricarbonylchromium derivatives has not been studied systematically. Nevertheless, these compounds offer considerable synthetic possibilities because of their particular chemical and stereochemical properties.

Recently, the quantitative liberation of arene ligands from tricarbonyl arene chromium derivatives has been accomplished simply by exposure of their ether solutions to sunlight.[2] The modification, on complexation, of steric and electronic factors and of the symmetry of the substrate ligand can thus be used to advantage in the synthesis of benzene derivatives difficult or impossible to prepare by other methods. In this communication, we report the resolution into enantiomers of 1-indanone- and 1-tetralonetricarbonylchromium and their use in the synthesis of new chiral molecules.

The $Cr(CO)_3$ group not only confers a third dimension on the aromatic precursor but also induces stereospecific exo nucleophilic attack on the alicyclic ring, thus creating new chiral centers. Quantitative liberation of the optically active organic ligand may then be easily accomplished at ambient temperature in air.

Resolution and Absolute Configuration of 1-Indanone- and 1-Tetralonetricarbonylchromium. Optically pure 1-indanone- and 1-tetralonetricarbonylchromium were obtained by oxidation of the corresponding 1-*endo*-indanoltricarbonylchromium and 1-*endo*-tetraloltricarbonylchromium with MnO_2 (yields around 70%). These secondary alcohols are themselves prepared in an optically active state by fractional crystallization of the cinchonidine salts of their acid succinates in acetonitrile. The maximal optical rotation values are given in Table I.

The optical purity and absolute configuration of these derivatives can easily be ascertained by displacement of the $Cr(CO)_3$ group from the active alcohols **1** and **5**.[4] Thus, from **1** ($[\alpha]^{22}D$ −60.7°), **3** is obtained (mp 72°; $[\alpha]^{22}D$ +34° (*c* 1.895)), having the *S* absolute configuration,[6] while **5** ($[\alpha]^{22}D$ −20°) yields **7** ($[\alpha]^{22}D$ −26.8° (*c* 6.04, benzene)) also having the *R* absolute configuration.[7] The ketones **4** ($[\alpha]^{22}D$ −334°,) and **8** ($[\alpha]^{22}D$ +870°) are thus optically pure and have the absolute configurations shown in Chart I. The same transformation sequence was made on both enantiomers.

From the chart, it is apparent the central chirality of **3** and **7** and the planar chirality[8] of **4** and **8** are interrelated, for the endo nature of alcohols **1** and **5** is now well established.[9,10] Thus, the two sorts of chirality, i.e., planar and central coexisting in **1** and **5**, are not independent of one another.

Preparation of Optically Active 2-Methyl-1-indanone and 2-Methyl-1-tetralone. This use of the $Cr(CO)_3$ moiety has been applied to other syntheses. The first example is the preparation of optically active 2-methyl-1-indanone and 2-methyl-1-tetralone. The obtention of optically active ketones remains tedious, and the difficulty increases when the asymmetric center α to the carbonyl group possesses a hydrogen atom,[11] thus adding risks of racemization. Scheme I shows how the use of tricarbonylchromium derivatives overcomes this difficulty.

The first reaction sequence illustrates the conversion of 1-indanonetricarbonylchromium (**4**) ($[\alpha]^{22}D$ −334°) to (2*R*)-2-methyl-1-indanone (**12**) ($[\alpha]^{22}D$ −42° (*c* 1.72, dioxane)) via 2-*exo*-methyl-1-indanonetricarbonylchromium (**10**) (mp 153–154°; $[\alpha]^{22}D$ −300° (*c* 0.92)). The second sequence shows the identical route used for the tetralone derivative **8** ($[\alpha]^{22}D$ +870°) giving **20** (mp 88°; $[\alpha]^{22}D$ +675° (*c* 1.06)), which then yields **22** ($[\alpha]^{22}D$ −51.2° (*c* 2,5-dioxane)), having the *S* absolute configuration.

These monomethylation reactions occur stereospecifically in an exo fashion. Products **10** and **20** have been com-